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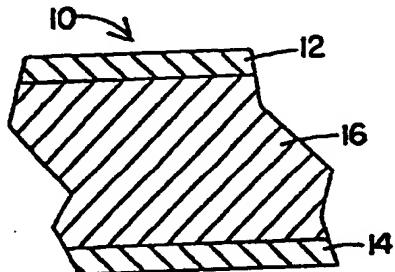
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(54) Title: VOIDED UNIAXIALLY ORIENTED FILMS

(57) Abstract

The invention is a uniaxially oriented film (10) comprising a polymer film (16) of at least one layer wherein within the layer is located a strata of voids. The voids cause the film to have an opacity greater than about 30 %. The invention is further a uniaxially oriented film comprising a polymer film of at least one layer wherein within the layer is located a strata of voids wherein essentially all of the voids are closed. The invention is further a process for orienting a voided film comprising the step of orienting a film consisting essentially of non-spherical void initiating particles wherein the particles cause the film to have an opacity greater than about 30 %. The invention is further the process for uniaxially orienting the above films.



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Title: **VOIDED UNIAXIALLY ORIENTED FILMS**INCORPORATION BY REFERENCE

The following patents are herein incorporated by reference: U.S. Patent Nos. 4,713,273; 5,186,782; and 5,435,963.

BACKGROUND OF THE INVENTION5 Field of the Invention

The invention is a uniaxially oriented film which is voided to the extent which allows for an unexpected improvement in its physical characteristics. The invention is further the use of these films in both pressure sensitive adhesive (PSA) and in-mold laminates and labels. The invention still further is the processes for the manufacture and use of these films, laminates and labels.

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Technology Review

It has been long known to manufacture and distribute biaxially oriented voided polymer films. These voided polymeric films have been used in a number of applications which require the polymeric films to provide a barrier to light transmission and provide for certain aesthetic affects, i.e., packaging materials, synthetic papers, label applications, laminates and tapes. Some of these applications require high opacity; and/or low water and/or oxygen transmission.

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It is known that voided polymeric films can be produced by the use of blowing agents in the polymer film materials, or by the biaxial orientation of a two-phase system. A biaxially oriented two-phase system consists of the matrix polymer and a void inducing or initiating particle or phase contained within the matrix polymer. The void initiating particle or phase being incompatible with the matrix polymer so upon biaxial orientation of the film the voids are initiated about the particle or phase.

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Two advantages of a biaxially oriented voided film structure are reduced light transmission (or opacity) and reduced materials usage. Opacity is important in applications such as packaging materials where high light transmission may result in a shorter shelf life for the substance being packaged

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(i.e., food, liquids, etc), and label materials where high light transmission may affect the aesthetics of the label (i.e., particular applications require materials with low light transmission characteristics). A voided film structure also provides for reduced materials usage for films of the same or similar gauge thickness resulting in overall reduced costs for producing the film.

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It is taught in the art that in order to achieve high opacity the films must be biaxially orientated. U.S. Patent No. 4,377,616 teaches in order to achieve high opacity it is necessary that the orientation conditions be such that the two major void dimensions must be significantly greater than the cross-sectional dimension of the void initiating particle, and that the optimum characteristics of opacity are achieved when the two major void dimensions are greater than 34μ (given void initiating particles from 0.1 to 10μ). It further teaches that the void initiating particles must be spherical, and that because of the comparative sphericity of the void initiating particles, the voids are closed cells.

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The art also points out the possible disadvantages of biaxially oriented voided films produced by orientation of incompatible two-phase systems. These disadvantages can include both a high water or oxygen transmission rate, and surface dust created by the void inducing particles. The high water or oxygen transmission rates are the result of the creation of a number of open or split voids created during the processing allowing for water or oxygen transport across the film. The high water or oxygen transmission rates may affect for example the very substances sought to be protected by the reduced light transmission of the voided packaging material. The high water or oxygen transmission rates may also prevent the use of these types of films in label applications where the transmission of water would affect the adhesives used to apply these labels or where the possibility exists for the bacterial growth spurred by warmth and humidity in these open or split voids. The surface dust is a result of the void initiating particles being able to escape from these open or split voids. The surface dust can affect the further processing of these films for the packaging or labeling markets by contaminating the production equipment and printing machinery.

It is an object of the present invention to present a voided film structure which is uniaxially oriented and has a unexpectedly high opacity. It is another object of this invention to present a voided film structure which is uniaxially oriented and wherein most of the cells or voids are closed allowing for low water and/or oxygen transmission. It is yet another object of this invention to present a process for preparing a voided film structure in which the void initiating particles or phases are non-spherical allowing for the use of non-traditional void-initiating materials (e.g., mica). It is still another object of this invention to present a process for producing an oriented film with unexpectedly increased stiffness. It is still another object of this invention to present a process for preparing the above film structures, and for the application of these films as label materials.

SUMMARY OF THE INVENTION

The present invention is an uniaxially oriented film comprising a polymer film of at least one layer wherein the layer is located a strata of voids, the voids causing the film to have an opacity greater than about 30%. The present invention is further a uniaxially oriented film comprising a polymer film of at least one layer wherein the layer is located a strata of voids wherein essentially all of the voids are closed. The present invention is still further a process for orienting a voided film comprising the step of orienting a film containing essentially non-spherical void initiating particles wherein the film has an opacity greater than about 30%. The present invention is still further the process for uniaxially orienting the above films, and applications of these films in label applications.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is one illustration of a film facestock embodying the invention.

Figure 2 is a sketch illustrating the steps of coextruding, hot-stretching and annealing used in the method of the invention.

Figures 3A-3D schematically illustrate certain manufacturing steps related to the environment of the invention.

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DETAILED DESCRIPTION OF THE INVENTION

The present invention is an uniaxially oriented film comprising a polymer film of at least one voided layer. The invention, however, is not limited to only a one layer film, but includes coextruded films of two or more layers, and laminates comprising two or more layers comprising at least one film layer attached by some adhesive means as well. Further layer(s) can consist of a film, paper, and other materials known in the art. The films can be used in a number of applications including but not limited to packaging materials and label materials. The films used for label applications can be used either for pressure sensitive adhesive label applications or for in-mold label applications.

Preferably, the film of the present invention contains two or more layers. For purposes of this application a two layer film contains a base layer and a skin layer, and a film with three or more layers contains two skin layers and a core which is made of one or more layers. More preferably, the film contains three layers.

While each of the layers of the film including the skins may contain voids. Preferably, the skin layer or layers contain essentially no voids. Essentially no voids preferably means that the skin layer contains less than about 10% by volume of voids, and more preferably less than about 3% by volume of voids. Preferably, one of the layers of the core contains voids, and more preferably the entire core contains voids.

The selection of materials for the skin layers, base layer and those layers of the core containing essentially no voids is dependent on the application of the film. The selection of materials for the voided layer or layers is further dependent on the void initiating particle or phase materials and on the process conditions necessary for creating the voids.

Materials for the skin layer (or layers) for pressure sensitive label applications and for the print surface in in-mold label applications include but are not limited to the following film-forming materials used alone or in combination such as polyethylene, metallocene catalyzed polyolefins, syndiotactic polystyrene, syndiotactic polypropylene, cyclic polyolefins, polyethylene methyl acrylic acid, polyethylene ethyl acrylate, polyethylene methyl acrylate,

5 acrylonitrile butadiene styrene polymer, polyethylene vinyl alcohol, polyethylene vinyl acetate, nylon, polybutylene, polystyrene, polyurethane, polysulfone, polyvinylidene chloride, polypropylene, polycarbonate, polymethyl pentene, styrene maleic anhydride polymer, styrene acrylonitrile polymer, ionomers based on sodium or zinc salts of ethylene/methacrylic acid, polymethyl methacrylates, cellulosics, fluoroplastics, polyacrylonitriles, and thermoplastic polyesters. Preferably, polypropylene is used in the skin layer (or layers) and more preferably a mixture of ethylene vinyl acetate/polypropylene is used.

10 Materials for the voided layer (or layers) and those essentially non-voided layers in the core or the base layer include but are not limited to meltable film-forming substances used alone or in combination such as polyethylene, polyethylene methyl acrylic acid, polyethylene ethyl acrylate, metallocene catalyzed polyolefins, syndiotactic polystyrene, syndiotactic polypropylene, cyclic olefins, polyethylene methyl acrylate, acrylonitrile, butadiene styrene polymer, polyethylene vinyl alcohol, polyethylene vinyl acetate, nylon, polybutylene, polystyrene, polyurethane, polysulfone, polyvinylidene chloride, polypropylene, polycarbonate, polymethyl pentene, styrene maleic anhydride polymer, styrene acrylonitrile polymer, ionomers based on sodium or zinc salts of ethylene/methacrylic acid, polymethyl methacrylates, cellulosics, fluoroplastics, polyacrylonitriles, polybutylene terephthalate (PBT), polyethylene terephthalate (PET) and thermoplastic polyesters.

15 The film can be manufactured by those processes known to those in the art such as casting or extrusion. The films are, however, preferably manufactured by a polymer extrusion or coextrusion process. The extrudate or coextrudate of polymeric film materials is formed by simultaneous extrusion from a suitable known type of extrusion or coextrusion die, and in the case of the coextrudate the layers are adhered to each other in a permanently combined state to provide a unitary coextrudate. A tie layer can be used when the materials of the layer (or layers) of the core, or materials of the core and the skin layer (or layers) do not sufficiently adhere or bond to each other when they are extruded together.

The cast or extruded film is then uniaxially oriented. The means for uniaxially orienting the film includes but is not limited to cold stretching, hot stretching, compression rolling, hot compression rolling, and a blown extrusion process. Preferably the material is hot stretched. If the film will have an application with further processing or service temperatures above room temperature, preferably the film is also heat set or annealed to provide for dimensional stability, i.e., prevents shrinking, relaxing or any distortion of the film. Preferably, the film thickness is less than about 7 mils. More preferably, the film thickness is from about 1 mil to about 6 mil. Most preferably, the film thickness is from about 2 mil to about 5 mil.

For purposes of this invention, uniaxial orientation means the film is oriented substantially in the direction of orientation and to a lesser degree in the relatively unoriented direction. This preferably means that the stiffness is the oriented direction (machine direction for extruded films) is greater than about 10 Gurley, and that the stiffness in the unoriented direction (cross direction for extruded films) is less than about 0.75 times the stiffness in the oriented direction. Still preferably the stiffness in the unoriented direction is less than about 0.6 times the stiffness in the oriented direction, more preferably less than about 0.5 times, and most preferably less than about 0.4 times.

The void initiating particle or phase material, as indicated above, should be, at least partially, incompatible with the core material, at least at the conditions of uniaxial orientation. Typical void initiating particles materials can be organic or inorganic. Examples of organic void initiating particles include but are not limited to polyamides; nylons; high density polyethylenes; polyesters such as polyethylene terephthalate; acetals; polypropylene homopolymer; and acrylic resins. Examples of inorganic void initiating particles include but are not limited to solid and hollow preformed glass spheres, metal beads or spheres; ceramic spheres; titanium dioxide; calcium carbonate; barium sulfate; chalk; silicon dioxide; and clay. The preferable inorganic void initiating particle materials are mica, clay and chalk; more preferable material is ceramic spheres; and the most preferable material is calcium carbonate. The preferred mean particle size of the void initiating particle or phase is from about 0.1 to about 30

um. The more preferred mean particle size of the void initiating particle or phase is from about 0.1 to about 12 um. The most preferred mean particle size of the void initiating particle or phase is from about 1 to about 3 um.

5 The void initiating particles can be of most any shape, i.e. spherical or non-spherical. Examples of non-spherical shapes of the void initiating particles include but are not limited to acicular (needle shaped), angular (sharply edged or roughly polyhedral), dendritic (of branched shape), fibrous (having the appearance of regularly or irregularly shaped threads), flaky (plate like), granular (approximately equidimensional but of irregular shape), irregular (lacking any symmetry), nodular (of rounded irregular shape), conical, and hemispherical.
10 The preferable particle shape is non-spherical. The more preferable particle shape is conical.

15 As indicated above, certain low cost filler materials such as calcium carbonate can be used as void initiating particles. Therefore, the greater the amount of void initiating particle, the lower the cost of materials in the film. Preferably, the void initiating particles or phase is present in an amount greater than about 30 weight percent of the voided layer prior to orientation. More preferably, the void initiating particles or phase is present in an amount greater than about 35 weight percent of the voided layer prior to orientation. Most
20 preferably, the void initiating particles or phase is present in an amount greater than about 40 weight percent of the voided layer prior to orientation.

25 The voided film layer is generally described as being a matrix material within which is located a strata of voids. From this it is to be understood that the voids create the matrix configuration. The term "strata" is intended to convey the understanding that there are a large number of voids creating the matrix and the voids are oriented so that the major dimension of the void is preferably aligned in correspondence with the direction of orientation of the polymeric film structure. After each void has been formed through the initiation of a particle, the particle may contribute little else to the system. This is because the refractive index of the particle can be close enough to the matrix material that it makes no contribution to opacity. When this is the case, the
30 opacity is principally a function of the light scattering affect which occurs

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because of the existence of voids in the system. The opacity of the system can be somewhat enhanced by the inclusion therein of opacifying pigment dispersed throughout. Preferably, the voids cause the film to have an opacity greater than about 30 percent. More preferably, the voids cause the film to have an opacity greater than about 50 percent. Most preferably, the voids cause the film to have an opacity greater than about 70 percent. Preferably, the uniaxially oriented film has an opacity greater than about 50 percent. More preferably, the uniaxially oriented film has an opacity greater than about 65 percent. Most preferably, the uniaxially oriented film has an opacity greater than about 80 percent.

A typical void in the film layer preferably is defined by having a major dimension in the uniaxially oriented or machine direction (X dimension) with minor dimensions in the non-oriented or cross direction (Y dimension) and in the Z dimension which corresponds to film or layer thickness.

It is preferable that the orientation conditions be such that the void is initiated and that the general integrity of the voids through growth is maintained. By this it is meant that during orientation which produces the X dimension, the temperature conditions must be such as to permit this dimension to form without any destruction of the voids in any of their dimensions. To reduce water or oxygen transmission across the film, preferably the majority of voids are closed cells without essentially any destruction of those voids considered to be closed cells. Still preferably, greater than about 60 percent of the voids are closed cells. More preferably, greater than about 70 percent of the voids are closed cells. Still more preferably, greater than about 80 percent of the voids are closed cells. Most preferably, greater than about 90 percent of the voids are closed cells.

As referred to above, the matrix polymer, copolymer or blends thereof and the void initiating particle must be incompatible. This term is used in the sense that the materials are two distinct phases. The void initiating particles or phase constitute a dispersed phase throughout a matrix which is preferably a lower melting material. The material upon orientation will become void filled with the void initiating particles positioned somewhere in the void.

As a result of the uniaxial orientation of the film structure described herein, in addition to opacifying the at least one voided layer of the structure, the orientation improves other physical properties of the composite layers such as crack resistance, tear strength, elongation, tensile strength and impact strength. When the voided film layer is combined with surface or skin layers, the resulting film can have a smooth high quality appearance with improved water vapor transmission characteristics and low oxygen transmission rate characteristics. This makes the film ideally suited for application to package food products, including liquids.

In one of the preferred embodiments, the film 10 shown in Figure 1 is a coextrusion consisting of a core 16 and top and bottom skin layers (12 and 14 respectively). The charges for the several layers are prepared for extrusion through the multifeed coextrusion die 18 as illustrated in Figure 2.

In this embodiment, the hot stretching is performed at a temperature equal to or above the softening temperature of the film and provides film orientation. During hot stretching the extrusion or coextrusion die is preferably maintained between from about 190°C to about 215°C, and more preferably at about 205°C. The extruded film is cast onto a casting roll 21 which is preferably maintained between from about 20°C to about 50°C, and more preferably at about 38°C, and is provided with an air knife 19. The film continues around the casting roll 21 and then passes to the chill roll 22 which is preferably maintained from about 20°C to about 50°C, and more preferably at about 38°C. The film continues around the chill roll, trains through the rolls 24, and enters the uniaxial (or machine) direction orientation unit (MDO) 25. The film is preferably moved at a rate of between from about 8 to about 13 feet per minute past all these rolls, and more preferably at about 8 feet per minute.

Within the MDO unit, the film is stretched and stiffened in the machine direction. The film is passed around a first pre-heat roll 26 and then around a second pre-heat roll 28. Both of these rolls are maintained at between from about 90°C to about 120°C, and more preferably at about 107°C, and at this point the film continues to move at between from about 8 to about 13 feet per minute, and more preferably at about 8 feet per minute. After leaving the

second pre-heat roll the film tracks on the slow draw roll 31 still preferably moving at between from about 8 to about 13 feet per minute, and more preferably moving at about 8 feet per minute. The slowdraw roll is maintained at between from about 95°C to about 140°C, and more preferably at 115°C.

5 The film is then pulled to the fast draw roll 32 which preferably advances the stock at the rate of between from about 56 to about 91 feet per minute, and more preferably at about 56 feet per minute. The fast draw roll is maintained at between from about 95°C to about 150°C, and more preferably at 118°C.

10 Therefore in this particular preferred embodiment described, the film is stretched sevenfold and is drawn down preferably to about 20% of its original thickness. Stretch ratios are preferably from about 4:1 to about 10:1, and more preferably are from about 5:1 to about 7:1.

15 In this particular embodiment, the film continues on its way preferably at a rate between from about 56 to about 91 feet per minute, and more preferably at a rate of about 56 feet per minute. As it leaves the pull-roll pair 31, 32, the stretched film is subject to severe shrinkage if it is heated while under little or no mechanical constraint. The polymer film is said to have a "memory" of its original length to which it tends to return when heated. The film is cured or annealed to remove this tendency by applying heat to the tensioned film at the 20 annealing roll 36 which in this embodiment is preferably maintained between from about 115°C to about 140°C, and more preferably at about 125°C. The film then passes directly to the chill roll 38. The roll 38 is preferably maintained at a temperature between from about 35°C to about 60°C, and more preferably at about 50°C. After leaving the chill roll 38 at the completion of the hot 25 stretch operation, the film may be taken up as a self-wound roll 39. The roll 39 may be conveniently transported and stored.

30 As mentioned earlier in the specification these films can be used in applications such as for packaging materials, synthetic papers, labels, laminates and tapes. The preferred application of these films, however, is in labels. While these films could foreseeably be used in any label application known to those skilled in the art, more preferably these films are used as either adhesive

preferably pressure sensitive adhesive labels (for facestock and/or liner) or as in-mold labels.

For pressure sensitive adhesive labels the film can be used as either a facestock or a liner, but preferably as a facestock. In the manufacture of label stock from the above described voided films and in accordance with the invention, liner or carrier stock 40 may be provided or a linerless construction can be produced. The liner or carrier stock 40 may comprise a multilayer liner made for example as disclosed in U.S. Patent No.4,713,273, the disclosure of which is incorporated herein by reference, or may be conventional liner or carrier consisting of a single paper or film layer which may be supplied in roll form. If it has not been previously provided with a release coating and does not itself include components to inherently generate a release surface at its adhesive-contacting face, the liner or carrier 40 may be coated with a release coating at station R, as shown in Figure 3A. If a release coating is applied, it is dried or cured following application by any suitable means known to those skilled in the art.

The release face of the release liner or carrier may be coated with a layer of pressure-sensitive adhesive for subsequent transfer of the adhesive to the facestock with which the liner or carrier is employed. When the facestock is combined with the liner or carrier, the adhesive is joined to the facestock. Later, the liner or carrier is removed to expose the adhesive, which now remains permanently joined to the facestock.

Thus, as indicated in Figure 3A, adhesive may be applied at station S following drying or cure of the release coat previously applied at station R. This may be a tandem coating operation, or the adhesive coating may be on a separate coating line. Alternatively, the adhesive may be applied at some later time prior to the joining of the release liner or carrier 40 with the facestock 50. The joining of the liner or carrier with a facestock 50 is diagrammatically illustrated in Figure 3B. Alternatively, the adhesive may be coated directly on the facestock 20 prior to combining of the facestock and liner or carrier.

5 In some applications, the adhesive may be an energy-activated (i.e., heat) or moisture-activated adhesive or a hot-melt adhesive such as used in in-mold label applications, as distinguished from a pressure-sensitive adhesive, in which case there may be no need for the provision of a release liner or inherent releasability such as is required when using a pressure sensitive adhesive. In some applications, the release coating may be directly applied to the print surface of the facestock.

10 The label facestock may be printed at a printing station prior to or after being die cut into individual labels. Further, the printing step may occur before or after the combining of liner and facestock. During printing, the film must remain in accurate register in order that image or text be of high quality, and between printing and die-cutting in order that image or text be located properly on the labels. The film is under tension during printing, and may be subjected to some increase in temperature depending on the types of inks used and their 15 method of cure. Therefore the label material must not stretch significantly in the machine direction. The machine direction tensile properties of the facestock film are particularly important when a polymeric film liner is used or when no liner is required.

20 Figure 4C diagrammatically illustrates the die-cutting of the facestock 50, at station I, into a series of spaced pressure-sensitive labels 64 carried by the release liner 40. This step may be performed by rotary cutting dies in a well-known manner (or can be performed by lasers or other methods known to those skilled in the art) and involves the stripping of the ladder-shaped matrix of waste or trim surrounding the formed labels when they are die-cut (the 25 "rungs" of the ladder representing the spacing between successive labels). The labels then remain on the liner in spaced relation with each other as shown. One failure mode in this operation involves poorly die-cut labels remaining with the matrix as it is stripped. In this mode, as release levels decrease, poor die-cutting is more likely to cause labels to stay attached to the matrix material and be removed from the liner during matrix stripping. Figure 4D illustrates the 30 application of the labels 64 to passing workpieces 66 by use of a peel back edge 68 to dispense the labels 64 by progressively removing the liner or carrier

from them to thereby expose the adhesive side 69 of the labels and project the labels into contact with passing workpieces 66. The workpieces 66 may either be flexible (deformable) substrates such as plastic bottles or rigid substrates such as glass bottles or other articles tending to have irregularities in the surface therefore requiring labels that are flexible and closely adhere to the surface without bridging local surface depressions.

It will be understood that the operations shown in Figures 3A to 3D may be done at different locations by different manufacturers, or they may be combined. For example, the steps of Figure 3A may be performed by a liner and adhesive manufacturer, the steps of Figures 3B and 3C may be performed by a label manufacturer on one continuous pass rather than being interrupted by a wind/unwind sequence as illustrated or separately by a laminator 3B and a convertor 3C, and the steps of Figure 3D may be performed by a container manufacturer or a packager of manufactured products.

When the films of the present invention are used for in-mold labeling, the film material, preferably consists of at least two (2) layers, a base containing the at least one voided layer, and an adhesive layer, and more preferably consists of at least three (3) layers, a print layer (which may be voided), a core containing the at least one voided layer and an adhesive layer. The adhesive layer can be coated onto the core by conventional coating processes or preferably can be coextruded with the film in the form of a heat seal layer. Preferably, the adhesive layer is tailored to be heat sensitive. The film material is printed then die or laser cut. The printed and cut label is placed inside the mold cavity during the molding process for producing a plastic container with the adhesive side facing the outside surface of the hot plastic container. As the plastic is molded, the heat activates or melts the adhesive on the label, and the label and the plastic container form a permanent bond.

Whether an in-mold label bonds to a container during the molding process without any problems is dependent upon many properties of the label material. One of these key properties is the insulative properties of the label and more particular of the base or core. This becomes more and more important as the label size increases. That is because as the label comes into contact with the

5 plastic container the heat generated from the container is used to activate or melt the heat seal layer of the label. If the base or core does not insulate the heat seal or adhesive layer, the labels tend to adhere poorly to the plastic container and may not adhere at all at certain locations. As the container cools down this tends to create bubbles or blisters in the label which are aesthetically unpleasing. Therefore, a label made of a film consisting of at least one voided layer is necessary for the proper application of in-mold labels on large size containers.

10 In order that persons in the art may better understand the practice of the present invention, the following Examples are provided by way of illustration, and not by way of limitation. Additional background information known in the art may be found in the references and patents cited herein, which are hereby incorporated by reference.

15

Examples

Examples 1-18

20 Examples 1-18 are samples of film typically used as in-mold labels. For in-mold labeling this film would typically be converted into labeling for application onto plastic containers during the process of forming these containers. Examples 1-18 were all three layer films containing a core and two skins which were produced by a coextrusion process. One skin is the print skin and the other skin a seal layer for bonding the label to the plastic container during the in-mold process.

25 Table I shows the composition of the core by weight percent of components. HPP was a homopolymer polypropylene sold by Union Carbide Corporation of Houston, Texas, under the product number 5A97. The 5A97 product has the following characteristics: a melt flow index of 3.9 grams/10 minutes; a melting point of 162°C; tensile strength at yield of 5350 psi; elongation at tensile yield of 8%; and a flexural modulus (1% secant) of 30 230,000 psi. The RnCopp was a random copolymer polypropylene was sold by Union Carbide Corporation of Houston, Texas, under the product name 6D20. The 6D20 random copolymer polypropylene has the following characteristics:

5 a melt flow of 1.6-2.2 grams/10 minutes; a density of 0.890 grams/cc; a tensile yield strength of 3600 psi; a yield elongation of 14%; a flexural modulus (tangent) of 130,000 psi; a vicat softening temperature of 134°C ; and a melting temperature of 147°C. The CaCO₃ is a concentrate of the void initiating particle and HPP with the following characteristics: the composition is polypropylene with 40 weight percent calcium carbonate mineral filler; the material has a melt index of 3.0 minimum to 6.0 maximum (ASTM D1238); ash of 40.0 +/- 2.0%; volatiles of 500 ppm max.; and a bulk density of 730 +/- 50 g/l.. The calcium carbonate concentration is sold by A. Schulman, Inc. of Akron, 10 Ohio under the product name Polyhatch PF92D. EVA is ethylene vinyl acetate and is sold by Quantum Chemical Corporation of Cincinnati, Ohio under the product name Ultrathene UE 631-04. The EVA material is a material which promotes higher temperature performance as well as adhesion to a variety of substrates. Ultrathene UE 631-04 contains a stabilizing additive package and 15 can also be used in compounded products where high filler loadings are required. The EVA material has the following properties: melt index 2.4 g/10 min.; tensile strength at break of 2150 psi; elongation at break of 710 percent; a 1% secant modulus of 5300 psi; a hardness (shore A) of 87; a ring & ball softening point of 174°C; and a peak melting point of 86°C.

20 The print skin layer of the three layer film consists of 50 weight percent EVA (described above) and 50 weight percent HPP (described above) was melted and mixed in a 1-1/4 inch extruder equipped with a screw of a L/D ratio of 24:1. This extruder was manufactured by Davis Standard of Pawcatuck, CT. The extruder contained three temperature zones which were maintained during melting and mixing at 205, 210 and 216°C respectively.

25 The core of the films of the compositions described above (see also Table I) was melted and mixed in a 2-1/2 inch extruder equipped with a screw of a L/D ratio of 28:1. This extruder was manufactured by Davis Standard of Pawcatuck, CT. The extruder contained four temperature zones which were maintained during melting and mixing at 216, 221, 227 and 232°C. The 30 calcium carbonate of the core material was dried prior to mixing in an oven

manufactured by Conair Franklin of Franklin, PA at 80°C for four hours to insure that the concentrate material contains minimal or no moisture.

5 **Table I.**
Composition of the Core
Weight Percent

	<u>Examples</u>	<u>HPP</u>	<u>RnCopp</u>	<u>CaCO₃</u>	<u>EVA</u>
10	1	75		25	
	2	50		50	
	3	60		40	
	4	45	15	40	
	5	30	30	40	
15	6	15	45	40	
	7	55		45	
	8	25	25	50	
	9	23	23	50	4
	10	17.5	17.5	50	15
20	11		50	50	
	12	25		75	
	13	35		65	
	14	23		73	4
25	15	18		78	4
	16			96	4
	17	23	23	50	4
	18	23	23	50	4

30 The heat seal layer consisted of 40 weight percent EVA (described above); 37.5 weight percent low density polyethylene; 20 weight percent of an antiblock concentrate; and 2.5 weight percent of an antistatic concentrate. The low density polyethylene was manufactured by Rexene Products of Dallas, TX under the product name LD Polyethylene PE 1017. The low density polyethylene material has good impact strength, heat seal and foaming characteristics. The LD Polyethylene PE 1017 has the following material properties (which are based on its product data sheet): melt index of 2.0 grams/10 minutes; density of 0.930 grams/cc; tensile strength at break of 1600 psi; a vicat softening point of 94°C; an elongation at break of 500 percent; a secant modulus of 32000 psi; and a shore D hardness of 50. The antistatic concentrate was manufactured

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by A. Schulman Inc. of Akron, OH under the product name Polybatch F-20. The Polybatch F-20 is an antiblock concentrate containing 20 weight percent natural silica based in low density polyethylene, and is designed for use in polyethylene applications. Both the particle size and the dispersion of this antiblock have been optimized to offer effective coefficient of friction values when used in conjunction with standard slip concentrates. The Polybatch F-20 material has the following material properties (which are based on its technical data sheet): melt index of the carrier resin of 9 +/- 4 grams/10 minutes; melt index of concentrate of 7 +/- 3 grams/10 minutes; ash (percent natural silica) of 20 +/- 2 percent; moisture retention (Karl Fisher @ 190°C) of 1000 ppm maximum; and pellets per gram of 46 +/- 5. The antistatic concentrate was also manufactured by A. Schulman Inc. of Akron, OH under the product name Polybatch VLA 55 SF. Polybatch VLA 55 SF is a specialty antistatic concentrate. The Polybatch VLA 55 SF material has the following material properties (which are based on its technical data sheet): melt index of the concentrate of 11-18 grams/10 minutes; and moisture retention (Karl Fisher @ 190°C) of 1000 ppm maximum.

The materials for the heat seal layer were melted and mixed in a 1-1/4 inch extruder manufactured by Davis Standard of Pawcatuck, CT with a screw of a L/D ratio of 24:1. The extruder contained three temperature Zones which were maintained at 205, 210 and 216°C respectively.

The three extruders feed a multilayer feedblock which then feeds a single manifold coathanger die. Both the feedblock, die and adapter pieces which connected the extruders, feedblock and die together were held at a constant temperature of 210°C. The three layer film was extruded onto a casting roll which is maintained at 38°C, and was provided with an air knife for further cooling the film. The film was then stretched uniaxially in the machine direction by being run through an orientation unit which orients the film in the machine direction (MD). The orientation unit consisted of a number of rolls the first of which were used for pre-heating the film prior to stretching. These rolls were maintained at 107°C so that a substantial portion of the thickness of the film is heated. The film was stretched between a slow draw roll (moving the film at 8 feet/second) and a fast draw roll (moving the film at 56 feet/second). All of

the samples in Example I were stretched or drawn down to approximately 5 mils which was approximately 22 percent of the original thickness of the film as it was extruded onto the casting roll. The stretched uniaxially oriented film was then cured (or annealed) by applying heat to the tensioned film stock at an annealing roll. The annealing roll was maintained at a temperature of 127°C. 5 The film was then passed onto a chill roll maintained at a temperature of 49°C.

The samples all ranged in thickness from approximately 3.8 to 5.3 mils.

Table II. shows the opacity, and elongation to break of these samples. The opacity was measured using the Tappi T 425 os-75 standard for measuring the 10 opacity of paper which is an accepted procedure in the label industry. The elongation at break was measured using ASTM Standard D882 for measuring the mechanical properties of polymer films. The results of the opacity measurements range from approximately 60 to 97 percent and show that films with unexpectedly high opacities can be produced by uniaxial orientation of 15 these films to create the voided structure.

Table II.
Physical Measurements of the Films

		Thickness (mils)	Opacity (%)	Elongation (%)	
				MD	CD
20	1	4.70	93.0	18	83
	2	4.84	93.2	18	55
	3	4.24	88.4	20	70
	4	4.28	85.5	20	280
25	5	4.26	86.7	22	290
	6	4.12	82.2	23	210
	7	4.70	92.6	20	68
	8	4.72	90.6	21	85
30	9	4.30	81.0	21	270
	10	3.84	61.2	20	280
	11	4.60	87.0	22	400
	12	5.74	96.9	18	86
35	13	5.30	95.6	19	79
	14	4.70	92.0		
	15	5.00	94.3		
	16	5.30	95.7		
40	17	4.20	83.7		
	18	4.10	84.9		

Table II and III show the mechanical properties of the films which are indicative of the degree of orientation. The Gurley values for stiffness were measured using TAPPI test method T543PM-84 and all normalized for 4 mil films. The modulus and ultimate tensile strength were measured using ASTM test method D882. The elongation, Gurley stiffness, modulus and tensile strength all indicate that these samples were uniaxially oriented. Further, the Gurley stiffness of the voided films were unexpectedly higher than the Gurley stiffnesses of similar unvoided films.

Table III.
Physical Measurements of the Films

	<u>Examples</u>	<u>Gurley</u>		<u>Modulus</u>		<u>Tensile Strength</u>	
		CD	MD	CD	MD (x1000 psi)	CD	MD (x1000 psi)
15	1	27	101	69	381	2.1	27.4
	2	24	91	63	375	2.1	27.3
	3	36	121	89	446	2.5	32.6
	4	37	115	98	418	2.9	30.9
20	5	35	110	92	427	2.6	33.1
	6	38	109	109	397	2.7	34.1
	7	30	106	80	376	2.1	28.3
	8	29	98	75	356	2.1	30.3
	9	33	106	94	376	2.4	31.9
25	10	34	92	79	329	2.4	30.4
	11	31	88	81	341	2.2	27.8
	12	20	82	45	278	1.4	19.3
	13	23	92	59	307	1.7	22.3

30 Example 19-32

Examples 19-32 are test samples of film typically used as pressure sensitive adhesive (PSA) label applications. For PSA labeling this film would typically be printed, die cut and matrix stripped then these labels would then be placed onto already formed plastic containers. Examples 19-31 were all three layer films containing a core and two skins which were produced by a coextrusion process. Table IV shows the composition of the core by weight percent of components. Descriptions for HPP, RnCopp, CaCO₃ and EVA are the same as those provided in Example 1. The TiO₂ was a filler and whitener

and was sold by A. Schulman, Inc. of Akron, Ohio, under the product name Polybatch White P8555-SD. The Polybatch White P8555-SD was a specialty white colored concentrate based on 50 weight percent of OPP grade homopolymer polypropylene, and 50 weight percent nitrile titanium dioxide.

5 The Polybatch P8555-SD has the following material characteristics: melt index of 8 +/- 2 grams/10 minutes; ash (TiO₂ content) of 50 +/- 2 percent by weight; moisture retention (Karl Fisher @ 190°C) of 500 ppm maximum; and a bulk density of 900 +/- 20 grams/liter.

10 Both of the skin layers (top and bottom) had the same composition, consisting of 50 percent by weight EVA, and 50 percent by weight HPP. The compositions were processed into a three layer film under conditions similar to that used for the three layer film above in Examples 1-18.

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Table IV.
Composition of the Core
Weight Percent

	<u>Examples</u>	<u>HPP</u>	<u>RnCopp</u>	<u>CaCO₃</u>	<u>TiO₂</u>	<u>EVA</u>
20	19	65		25	10	
	20	65		25	10	
	21	65		25	10	
	22	65		25	10	
	23	63		23	10	4
25	24	48		38	10	4
	25	38		48	10	4
	26	28		58	10	4
	27	18		68	10	4
	28	18		68	10	4
30	29	18		68	10	4
	30	9	9	68	10	4
	31	24	24	38	10	4

35 Table V. shows the samples all ranged in thickness from approximately 1.6 to 2.6 mils. Table V. further shows the opacity of these samples. The opacity was measured using the Tappi T 425 os-75 standard for measuring the opacity of paper. The results of the opacity measurements range from approximately 80 to 92 percent and show that films with unexpectedly high

opacities can be produced by uniaxial orientation of these films to create the voided structure.

5 **Table V.**
Physical Measurements of the Films

	<u>Example</u>	<u>Thickness</u> <u>(mils)</u>	<u>Opacity</u> <u>(%)</u>
10	19	2.62	88.1
	20	~2.00	84.1
	21	~1.75	82.5
	22	~1.64	80.5
	23	~2.25	80.5
	24	~2.25	85.1
15	25	~2.25	87.5
	26	~2.25	89.3
	27	~2.25	90.0
	28	~2.25	92.3
	29	~2.50	91.2
	30	~2.25	92.6
20	31	~2.25	85.2

25 Table VI shows the mechanical properties of the representative samples of these films which are indicative of the degree of orientation. The Gurley values for stiffness were measure using TAPPI test method T543PM-84. The modulus and tensile strength were measured using ASTM test method D882. Again, the Gurley stiffness, modulus and tensile strength all indicate that these 30 sample were uniaxially oriented. Further, the Gurley stiffness of the voided films were unexpectedly higher than the Gurley stiffnesses of similar unvoided films.

Table VI.
Physical Measurements of the Films

5	<u>Example</u>	Gurley		Modulus		Tensile Strength	
		<u>CD</u>	<u>MD</u>	<u>CD</u>	<u>MD</u>	<u>CD</u>	<u>MD</u>
	19	14	44(actual)	106	525	3.0	39.4
	22	3.5	11(actual)	117	640	2.9	41.1

10 This example is used to organize the samples from Examples 1 to show that the weight percentage of void initiating particle can exceed 25 percent by weight of the total composition without affecting opacity or the ability to orient the material by uniaxial orientation, and shows the unexpected result of being able to produce a voided composition at such high void initiating particle concentrations.

Table VII.
Opacity as a Function of Increasing Weight Percentage
of Void Initiating Particles

20	<u>Example</u>	<u>HPP</u>	Composition (Weight Percent)		<u>EVA</u>	Opacity (%)
			<u>CaCO₃</u>	<u>EVA</u>		
25	1	75	25			93.0
	3	60	40			88.4
	7	55	45			92.6
	2	50	50			93.2
30	13	35	65			95.6
	14	23	73	4		92.0
	12	25	75			96.9
	15	18	78	4		94.3
	16		96	4		95.7

5

It is understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the scope and spirit of the present invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the description set forth above but rather that the claims be construed as encompassing all of the features of patentable novelty which reside in the present invention, including all features which would be treated as equivalents thereof by those skilled in the art to which the invention pertains.

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Claims

1. A machine direction oriented film comprising a polymer film of at least one layer
wherein the layer is located a strata of voids and the voids causing the film to have an opacity greater than about 30% and
5 wherein the film is less than about 7 mils in thickness.
2. The film of claim 1, wherein the polymer film has face and opposite sides and a pressure sensitive adhesive is combined with the film at the opposite side to form a laminate.
- 10 3. The film of claim 2, wherein the laminate is combined with a release liner.
4. The film of claim 1, wherein the polymer film is a coextrudate of cojoined layers.
- 15 5. The film of claim 4, wherein the coextrudate of cojoined layers comprises a core or base along with at least one relatively thin skin layer.
6. The film of claim 1, wherein the film contains a voiding agent comprising greater than about 25% by weight of the voided layers.
- 20 7. The film of claim 6, wherein the voiding agent comprises greater than about 32% by weight of the voided layers.
8. The film of claim 7, wherein the voiding agent comprises greater than about 35% by weight of the voided layers.
- 25 9. The film of claim 1, wherein the film contains a voiding agent comprising essentially non-spherical particles.
10. A film comprising a polymer film having a machine direction and cross direction of at least one layer
wherein the layer is located a strata of voids, the voids causing the film to have an opacity greater than about 30%, and
30 wherein the film is less than about 7 mils in thickness and the machine direction stiffness is greater than about 10 Gurley and the cross direction stiffness is less than about 0.75 times the machine direction stiffness.

11. The film of claim 10, wherein the polymer film has face and opposite sides and a pressure sensitive adhesive is combined with the film at the opposite side to form a laminate.

5 12. The film of claim 11, wherein the laminate is combined with a release liner.

13. The film of claim 10, wherein the polymer film is a coextrude of cojoined layers.

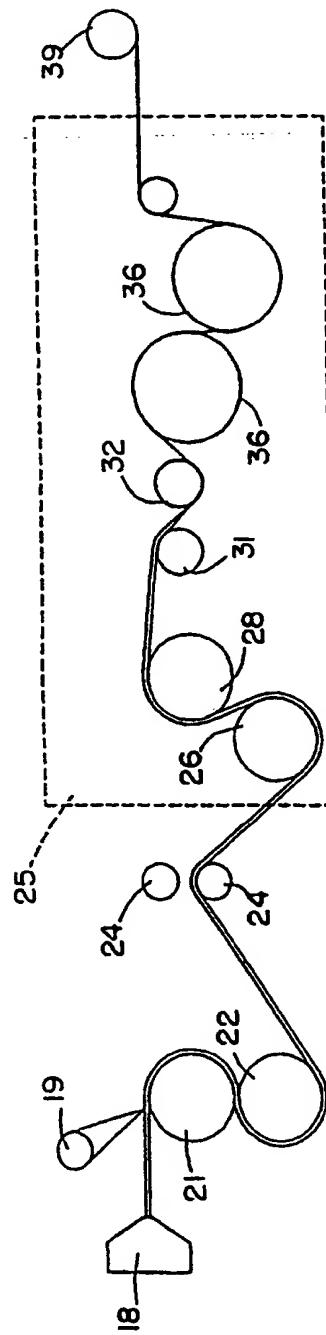
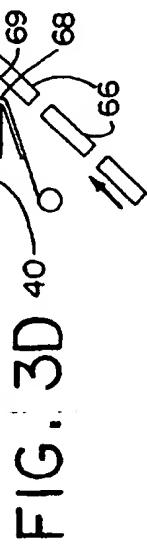
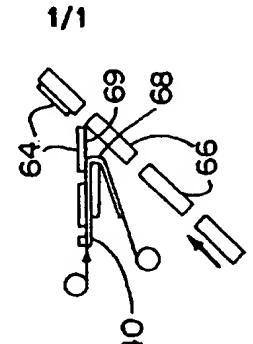
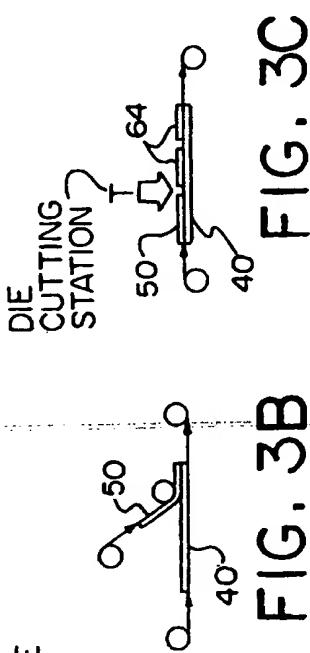
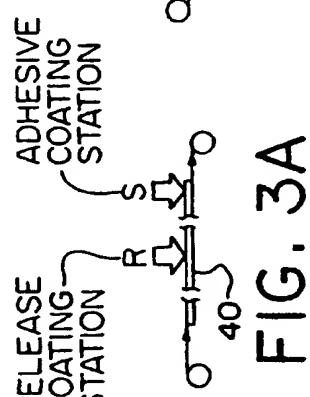
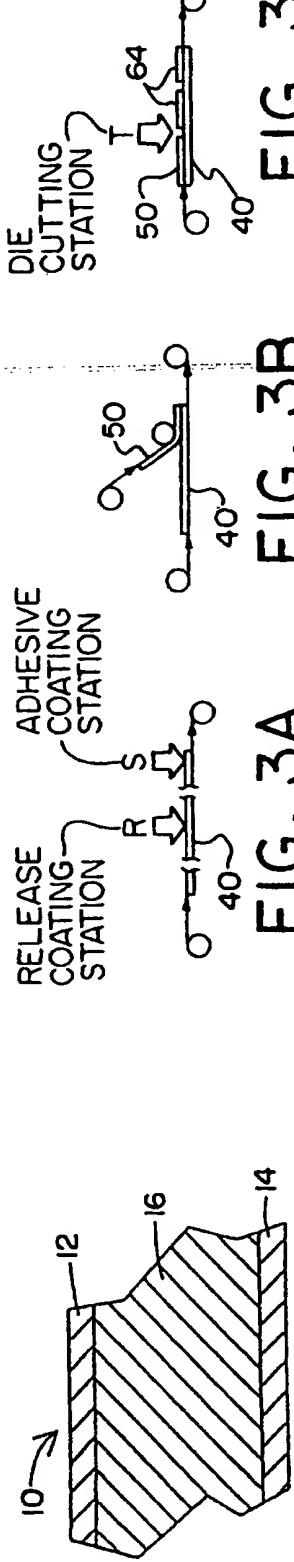
14. The film of claim 13, wherein the coextrude of cojoined layers comprises a core or base along with at least one relatively thin skin layer.

10 15. The film of claim 10, wherein the film contains a voiding agent comprising greater than about 25% by weight of the voided layers.

16. The film of claim 15, wherein the voiding agent comprises greater than about 32% by weight of the voided layers.

15 17. The film of claim 16, wherein the voiding agent comprises greater than about 35% by weight of the voided layers.

18. The film of claim 10, wherein the film contains a voiding agent comprising essentially non-spherical particles.



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/02141

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B32B 3/26, 5/30

US CL :428/40, 314.2, 314.4, 317.3, 317.9, 323, 354, 910

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/40, 314.2, 314.4, 317.3, 317.9, 323, 354, 910

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,194,324 A (POIRIER) 16 March 1993, see entire document.	1-8, 10-17 ----- 9, 18
X	US 5,176,954 A (KELLER ET AL.) 05 January 1993, see entire document.	1-18

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"B"	earlier document published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reasons (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed	

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